1.0

1.1

1.25 1.4 1.6

2.8 2.5

3.2 2.2

3.6

4.0 2.0

1.8
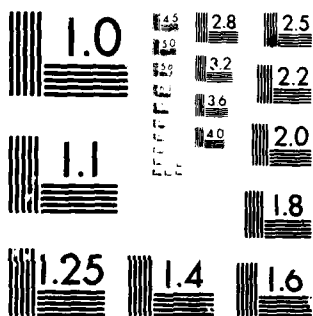
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

TRANSPORT OF WATER, DISSOLVED
SUBSTANCES, HEAT AND ELECTRIC
CURRENT THROUGH SHALES AND
CLAY-RICH SEDIMENTS

FINAL REPORT

DONALD L. GRAF
WILLIAM M. BENZEL
PAUL HAYDON

FEBRUARY 4, 1980

U.S. ARMY RESEARCH OFFICE

GRANT DAAG29-77-G-0011

DEPARTMENT OF GEOLOGY
UNIVERSITY OF ILLINOIS
AT URBANA-CHAMPAIGN

APPROVED FOR PUBLIC RELEASE
DISTRIBUTION UNLIMITED

80 2 25 036

TRANSPORT OF WATER, DISSOLVED SUBSTANCES, HEAT AND ELECTRIC CURRENT THROUGH SHALES AND CLAY-RICH SEDIMENTS

FINAL REPORT

DONALD L. GRAF
WILLIAM M. BENZEL
PAUL HAYDON

FEBRUARY 4, 1980

U.S. ARMY RESEARCH OFFICE

THE FINDINGS IN THIS REPORT ARE
NOT TO BE CONSTRUED AS AN OFFICIAL
DEPARTMENT OF THE ARMY POSITION,
UNLESS SO DESIGNATED BY
OTHER AUTHORIZED DOCUMENTS.

TABLE OF CONTENTS

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
14207.1-GS		

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
Transport of water, dissolved substances, heat and electric current through shales and clay-rich sediments	Final rept. Oct. 11, 11 oct 76 - 10 oct 79
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
Donald L. Graf, William M. Benzel, and Paul Haydon	Grant No. DAAG29-77-G-0011

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
University of Illinois at Urbana-Champaign (Department of Geology) Urbana, Illinois 61801	

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
U.S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709	February 4, 1980
	13. NUMBER OF PAGES
	17

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report)
	Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE NA

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Brine, clay, smectite, shale, salt rejection, clay membrane, ultrafiltration, osmosis, nonequilibrium thermodynamics, sodium chloride, calcium chloride, hydrothermal apparatus, high pressure apparatus

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Two 300-ton capacity load frames have been constructed for monitoring the cited fluxes across constructed clay cakes of known mineralogy, fabric, and particle-size range. One of the load frames is enclosed in an air bath for operation to 250° C., and precipitation-hardenable stainless steel and Ni-base alloy have been used extensively in both for corrosion resistance to concentrated salt solutions and for strength at temperature. Novel design
(continued)

(Block 20 continued)

elements include a mechanism for driving upstream brine back and forth between two high pressure reservoirs to minimize salt buildup at the brine-clay cake interface, and a downstream sampling cell that allows fluid to be collected at a selected pressure. Thus, lithostatic pressure, hydrostatic pressure, and hydrostatic pressure gradient across the clay cake may be varied independently.

At room temperature, a hydraulic differential of 1000 p.s.i. across clay cakes 1.5 to 2.5 cm thick and 9.15 cm in diameter held under 5,000 p.s.i. confining pressure gives approximately 1.0 ml fluid flow per day. (hydraulic conductivity of about 3 x 10^{-12} cm/sec). Salt rejection efficiency is 26% for one molal (Na,Ca)Cl solution, and effluent Ca/Na ratio increases by 24%, but salt rejection efficiency for a 5.5 molal solution of the same Na/Ca ratio is only 8.4%.

19 references.

INTRODUCTION

The long-range goals of this research program are (1) to measure experimentally the magnitudes of the fluxes of water, dissolved substances, heat and electric current across smectite and illite clay layers, under imposed gradients of fluid pressure, chemical activity of dissolved salts, temperatures, and electrial potential, from atmospheric conditions through the diagenetic range to approximately $250°$ C. and 2 kb. confining (lithostatic) pressure, and (2) to relate these measurements to existing theories, including in particular the formalism of nonequilibrium thermodynamics, and to augment such theoretical expressions if possible. The principal earth-surface applications are to soil physics and to a variety of civil engineering concerns involving slope and foundation stability. At depth in sedimentary basins, fluid flow across shales has been invoked in theories of hydrocarbon generation and migration, as a possible explanation for a variety of phenomena of interest to petroleum engineering such as overpressuring and electrical self-potentials, and as a factor to be considered to evaluating the feasibility of deep-hole radioactive waste disposal. The physical characteristics of the clay layer, such as layer thickness, clay-flake size, clay-flake orientation (fabric), and change of fabric and particle size within a layer (composite membrane) also need to be evaluated.

This research is strengthened by the results that are accumulating from three related but non-USARO-funded research efforts: (1) measurement of mutual diffusion coefficients in concentrated binary salt solutions (Rard and Miller, 1979a, 1979b), and development of improved theoretical models for predicting mutual diffusion coefficients in more complex salt

solutions (Anderson and Graf, 1978); (2) measurement of adsorbed cation populations on clay minerals in contact with chloride brines over the range of diagenetic conditions (Stephens, 1974, Benzel, 1978); and (3) measurement of the amount of interlayer water in smectite as a function of pressure, temperature, and brine composition over the diagenetic range (Graf, 1974).

During the period of this grant, two large and complex membrane presses were designed, built, and put into operation at room temperature. Detailed techniques were devised for sedimenting clay cakes of known particle-size and fabric and for impregnating these cakes, cutting out volumes of known orientation, and determining fabrics by powder X-ray diffraction. An initial pair of transport experiments has been completed at room temperature, in order to tie in with existing literature and to determine the run time required to reach steady state. Sample collection and analysis techniques for stable isotope determination have been chosen.

Two papers are currently in preparation: (1) a description for a scientific instrument journal of the membrane press design must await successful completion of one or two runs above room temperature on the press that is enclosed in an air bath, in order to be sure that the temperature-control system is adequate; and (2) Donald L. Graf has accepted an invitation to present before the International Association of Scientific Hydrologists in Paris this summer, and to publish in Journal of Hydrology, a discussion of the potential usefulness to this group of better knowledge of diffusion in brines and of clay-membrane transport behavior.

DESIGN AND CONSTRUCTION OF
EXPERIMENTAL APPARATUS

Two large membrane presses with suitable auxiliary devices for clay-sample retention, fluid injection, stirring of fluid at pressure, and collection of fluid at pressure have been designed and constructed. One press is for room temperature operation, the other for use at temperatures up to about 260° C., at which deterioration of Teflon O-ring seals might be expected to commence. A description of the latter press suffices for both.

The load frame consists of four 3-inch diameter vertical rods, 52" long, attached through holes near the corners to horizontal, stationary top and bottom plates approximately 27" by 17" by 3" thick. A traveling center platen is 2" thick. These load-frame elements are of 17-4-PH stainless steel, the plates machined from special castings (Coulter Steel and Forge Co., Emeryville. California), and all elements heat-treated after machining by Indiana Metal Treating, Indianapolis, Indiana. The traveling platen is driven by a commercially available 300-ton ram (Enerpac, Butler, Wisconsin), in which our machine shop has replaced the manufacturer's seals with Teflon and brass elements. The hydraulic fluid used is Dow Corning 200/20 cs. silicone.

The entire load frame is enclosed in an air bath to prevent transport contributions from local thermal gradients. The air bath is a double-walled shell, enclosing a 2-inch thick layer of magnesium oxide, from which one vertical wall can be removed for equipment repair and sample loading. There are six planar 800-watt heating elements (Lindberg, Watertown, Wisconsin) fastened to the interior of the shell, controlled by a RI Thermac Series 6000 temperature controller (Carvel Engineering, Schaumberg, Illinois). The shell and press rest on 1/4" thick basal

plate of asbestos board, which is in turn underlain by a layer of 2 1/2" thick fire bricks (A. P. Green Refractories Co., Peoria, Illinois) to minimize heat loss to the floor.

The clay layer lies between two sheets of filter paper (Millipore Corp., Bedford, Mass.; 0.6-micron diameter particle-retention Polyvic paper for temperatures up to about 65° C.; Teflon paper with 5.0 micron diameter particle retention for temperatures up to 260° C.). We have also tried Nuclepore filters (General Electric Co., Pleasanton, California), irradiated plastic with very uniform 0.2 micron diameter holes, but its temperature tolerance is limited. Backing the filter paper sheets are porous alumina plates (Norton Co., Worcester, Mass.; #AN 788, 0.1 micron diameter particle retention), and then a second set of porous plates (Norton's AN 889, 5 micron diameter particle retention), and finally pistons of INCONEL X-750. The central six inches of this vertical train, piston-alumina-clay-alumina-piston, is enclosed in a thick-walled cylinder of INCONEL X-750 (O. D. 10", I. D. 3.9", length 10"; custom forging by Coulter Steel and Forge Co., Emeryville, California; heat-treated by Indiana Metal Treating, Indianapolis, Indiana). Shrunk-fit into the cylinder is a precision-ground, high purity alumina refractory liner with a wall thickness of about 0.15" (McDanel Refractory Co., Beaver Falls, Pa.; Mix #998; grinding by INSACO, Quakertown, Pa.). It is electrically insulating, strong in compression, and should not readily be attacked by solutions already saturated in alumina from contact with clay.

A pair of 1/8" diameter holes in the upstream piston (deep-hole drilling by Meteor Corp., Loves Park, Illinois) permit brine to be circulated through the higher-porosity alumina plate while maintaining the desired experimental hydraulic pressure. There is one such hole in the downstream piston for drainage at pressure. An additional pair of holes in each piston will permit introduction of lead wires to planar Ag-AgCl electrodes for measurement of, or imposition of, electrical potentials. The holes are at present plugged with O-ring-sealed metal rod, but for electrical-potential studies the lead wire will be electrically insulated by ball-and-socket-type ceramic beads (Barber-Colman, Rockford, Illinois), except for the region extending through the high-pressure seal (slightly below the piston face), where a section of magnesium-oxide insulated wire swaged into an INCONEL sheath will be used (ARi Industries, Franklin Park, Illinois).

Corrosion-resistant high-pressure tubing of INCONEL X-750, O. D. 1/4", I. D. 0.084" was obtained by special order (Tube Methods, Bridgeport, Pa.). The high-pressure valves are of special design (Pressure Products Industries, Hatboro, Pa.) so that (1) corrosive brine touches only Haynes Alloy #25 surfaces in the valves, and (2) the valve stem packing is on the outer wall of the air bath, with provision for water cooling, and the stem is long enough to extend through the air bath wall to reach a high-pressure line attached to the inside wall. Valve packing is glass-loaded Teflon. Large-diameter Heise gauges (Dresser Industries, Newtown, Conn.) with Bourdon tubes of 403 stainless for accurate pressure response are used, but the Bourdon tubes are oil filled to prevent damage to this not particularly corrosion-resistant alloy.

An auxiliary system modified from an earlier design in this Department by F. A. Donath and L. S. Fruth for fluid injection at high pressure and over a wide range (6 to 8 orders of magnitude) of low flow rates consists of two geared shafts with a movable connecting gear and a variable-speed motor (B and B Motor and Control Corp., New York City). This assembly drives an INCONEL X-750 piston into an approximately 50 ml. volume INCONEL X-750 high-pressure chamber and thereby forces fluid into the high-pressure tubing network.

An auxiliary unit designed by us with the help of L. S. Fruth, John Bauerle, and Donald Dodson disperses the dissolved-salt buildup behind the clay cake into a larger fluid volume at the same pressure. It consists of two INCONEL X-750 high pressure reservoirs, each of about 85 ml. volume, linked by a double-ended piston driven by a reversible motor (Dayton split-phase gearmotor, W. W. Grainger Inc., Chicago, Illinois), which is actuated by a timer (Dual-Trol timer, Industrial Timer Corp., Parsippany, N. J.) for five minutes every three hours. The remaining two ends of the reservoirs are connected by high-pressure tubing to the appropriate fittings on the upstream piston. This unit has been placed outside the air bath, for easier maintainance, so that in order to minimize brine temperature change during the stirring intervals, it has been necessary to place an approximately 10 ml. volume high-pressure reservoir ("rod bomb") of Haynes Alloy #25 inside the air bath in each of the lines leading from the high-pressure stirring unit to the upstream piston. The storage volume of the high-pressure stirring unit has been further increased by making the double-ended piston short enough so that it extends a maximum of 3 3/4" into either of the high-pressure chambers, which are 6 3/4" long.

An auxiliary unit for collecting liquid effluent at selected fluid pressure, designed by us with the help of L. S. Fruth, John Bauerle, and Donald Dodson, consists of a pressure vessel made of elements of INCONEL X-750 and 17-4-PH. The vessel has a small-diameter, approximately 10 ml. volume chamber in one end, a large-diameter chamber in the other, and an internal piston with differnt diameters on its two ends. The large-diameter chamber is connected directly to a large tank of nitrogen gas at some selected fraction of full tank pressure. The ratio of piston areas then defines the fluid pressure that will move the piston and allow the small-diameter chamber to fill, and PVT relations for the large volume of gas assure that liquid-sample accumulation will be at essentially constant pressure. If the line back to the clay cake is valved off and a 10 ml. glass or plastic vial pushed over an O-ring seal on an appropriately machined exit fitting, then the vial can be evacuated, the exit valve opened, and nitrogen gas pressure will drive the sample piston back to expel accumulated liquid sample into the vial.

PREPARATION AND DEFINITION
OF CLAY FABRICS

Clay flakes typically have positively-charged edges and negatively-charged surfaces (see, e.g., van Olphen, 1977), so that changing clay fabric alters the distribution along a particular pore not only of pore diameter but also of positively- and negatively-charged mineral surfaces. It is hardly surprising, therefore, that there should be increasing interest in the effects of clay fabric upon engineering properties (e.g., Bennett et al., 1977: Calladine, 1973; Mahmood and Mitchell, 1974; Martin and Ladd, 1975).

The fabrics of some well-consolidated Paleozoic shales change from parallel-flake to jumbled-flake (card-house fabric) within tens of feet laterally (Parham and Austin, 1969; W.E. Parham, pers. comm.). These fabrics appear to date from the time of sediment deposition, rather than being consequences of compaction, and mild metamorphism (crystallization) is required to alter them. Observations such as these have led to speculation about the effect of clay fabric upon shale transport behavior, which should in turn affect the migration of hydrocarbons from shale source beds, the content of U and other metals in black shales, and the suitability of shales as hydraulic seals for retaining radioactive wastes.

We have focused our initial transport experiments upon smectite, which is attractive both because it is a geologically abundant clay mineral in the thick sedimentary sequences of interest to us, and because it has a high cation exchange capacity and should therefore demonstrate membrane effects to a maximum degree. Smectite flakes are often unusually small and ragged, even for clay minerals, which makes it more difficult to sediment a range of fabrics.

Mr. Benzel has been able to prepare a smectite cake with card-house fabric by sedimenting from a 1.01 molal (Na,Ca)Cl solution, with which the clay had first been allowed to equilibrate. He obtained a parallel-flake cake by repeated washing of smectite in distilled water until it dispersed, followed by sedimentation from that liquid.

We have determined fabric character by impregnating the clay cake with Carbowax 6000 (Union Carbide's polyethylene glycol), cutting a cube which has as one pair of faces the top and bottom of the cake, and collecting diffraction data from the differently oriented faces according to the method of Meade (1961). The parallel-flake cake had a Meade parameter of 5.6, the card-house fabric gave 1.2. It is noteworthy that these fabrics were unaltered by the 5,000 p.s.i. piston pressure applied in a small laboratory-bench press during fabrication of the cakes.

The smectite cake currently being used in Mr. Benzel's membrane-press experiment was prepared as described above to yield a card-house fabric, as was that which Mr. Haydon is using, except that his was equilibrated with and sedimented from a 5.45 molal (Na,Ca)Cl solution. X-ray fabric determinations of these particular cakes will be made after the transport experiments using them are completed, but it seems reasonably certain that they will be found to be highly jumbled fabrics.

One of Mr. Benzel's next transport experiments will utilize a parallel-flake cake, to determine how large is the effect of fabric upon salt-rejection efficiency and selective cation transport. If the effect is comfortably above experimental uncertainty, we may explore the effect of a few more subtle fabric variations. Among the card-house fabrics, depending upon the salinity and cationic composition of the brine, floc

size and organization should vary. For fabrics toward the parallel-flake end of the range, we will attempt to employ an unpublished method devised by R. C. Reynolds of the Department of Earth Sciences, Dartmouth College, to describe the distribution of flake orientations with regard to the c - axis.

Mr. Benzel is preparing clay cakes using the 0.25-2 micron diameter size fraction of the smectite from Chambers, Arizona, for a series of room temperature experiments testing the effect upon transport of physical parameters such as layer thickness, particle size and fabric. The clay is the same one for which Mr. Benzel measured Na^+/Ca^{++} adsorption selectivity (Benzel, 1978), and it is mineralogically very pure. In his first run, he observed a hydraulic conductivity of 2.51×10^{-12} cm/sec, a salt rejection efficiency of 26%, and an increase in Ca/Na atomic ratio of 24% in the effluent when a (Na,Ca)Cl solution of 1.01 molal total salinity was forced through a 2.5 cm thick cake with card house fabric. Compaction pressure was 5,000 p.s.i., upstream fluid pressure 2,800 p.s.i., and downstream fluid pressure 1,800 p.s.i.

Mr. Haydon is using the 0.25-2 micron diameter size fraction of the smectite from Olmsted, Illinois, for experiments in which the same cake is left in the membrane press and other variables are held constant, but transport is measured successively at several temperatures between room temperature (20°C) and 250° C. This clay is representative of the river-borne input to the Gulf Coast, and is not monomineralic; the principal clay mineral is actually an interlayered illite-smectite, and there are small amounts of organic matter and other clay minerals present. In his initial experiment at 25° C. Mr. Haydon observed a hydraulic conductivity of 3.36×10^{-12} cm/sec, a salt rejection efficiency of 8.4%, and a 0.4% decrease in Ca/Na atomic ratio in the effluent when a (Na,Ca)Cl solution of 5.55 molal total salinity was forced through a 1.5 cm thick

cake with card-house fabric. Pressures were the same as in Mr. Benzel's run.

Mr. Haydon chose the salinity and cation ratio of his brine to be representative of Gulf Coast pore waters at 10,000 feet depth in normally-pressured regions. Mr. Benzel diluted this solution to approximately one-fifth its original concentration, to yield a brine more realistic for near-surface environments, about half again more saline that sea water but retaining its (Na,Ca)Cl character so that results from the two presses might reinforce each other in at least a qualitative sense. The compaction pressure being used in Mr. Haydon's first cycle of experiments is more appropriate for 5,000 feet depth than 10,000, but he will increase it substaintially in the second cycle.

The hydraulic differential of 1,000 p.s.i. across the cakes in these two experiments gave a liquid throughput of approximately 1 ml. per day. It was only after the passage of 25 to 30 ml. of fluid that the system reached steady state, a major limitation upon the rate of data collection. The values for salt-rejection efficiency and change in Ca/Na atomic ratio cited here differ moderately from those cited in the 6-monthly report for the latter half of 1979 because of data reduction errors discovered in a project review.

For comparision, Kharakha and Smalley (1976) forced an approximately 0.1 molal chloride solution, containing Na^+, Ca^{++}, and other cations, across a 0.31 cm. thick bentonite cake at room temperature. Compaction pressure was 7,000 p.s.i., upstream fluid pressure 1,580 p.s.i., downstream fluid at atmospheric pressure. The salt-rejection efficiency was 52% and the Ca/Na atomic ratio increased by 5.2% in the effluent. The strikingly low salt rejection efficiency seen by Mr. Haydon must for the

most part be a result of the high salinity of his input solution, rather than of the mineral impurities in his sample. The reasons for the observed Ca/Na atomic ratio changes are less obvious.

CHEMICAL ANALYSIS

Mr. Benzel's liquid effluent samples are diluted approximately 830 times, Mr. Haydon's by a factor of about 2860, in order to bring the concentrations of both Na^+ and Ca^{++} within the linear portion of the atomic absorption calibration curve obtained by running a series of standard solutions that encompass the expected range of experimental solution compositions after dilution. Standards also contain 2000 p.p.m. CsCl in order to inhibit ionic complexing. The spectrometer being used is a Perkin-Elmer Model 306 at the Illinois State Geological Survey on campus.

Cation exchange capacity measurements are in progress, using X-ray fluorescence to determine adsorbed Sr^{++} concentration, for the 0.25-2 mircron fractions of the two smectites. There is at least one published value for each clay, but some difference might be expected among multiple whole-clay samples from the same deposit, as well as among different size fractions of the same sample.

FRACTIONATION OF STABLE ISOTOPES OF HYDROGEN AND OXYGEN IN BRINE WATER DURING ULTRAFILTRATION

Citing experimental results for a variety of systems in the pure chemistry literature, Graf et al. (1965) and Hitchon and Friedman (1969) attributed small differences in stable hydrogen and oxygen isotopic composition of selected pairs of subsurface brines to fractionation during passage through the micropores of shale. The effluent is isotopically lighter, affording a criterion for direction of water flow.

Coplen and Hanshaw (1973) made two experimental runs at room temperature that verified the predicted fractionation in clay-water systems. As with all clay-membrane experiments, the time required to come to steady state was considerable.

The experiments of this project bring clay-water systems to steady state in order to measure other parameters, and it requires only modest additional amounts of run time to collect two 2-ml downstream samples and to extract two 2-ml samples from the upstream reservoir, so that the oxygen and hydrogen isotopic fractionations can both be determined. We are about to collect such sets of samples from the first two runs.

It would be difficult to be certain of extracting all the water from small samples of high salinity. We propose instead to equilibrate CO_2 with the brine sample as collected, and then to correct for the ion-hydration effects that are included in the isotopic composition obtained. These effects have been calibrated by Sofer and Gat (1972) and Truesdell (1974) for a range of solution compositions and temperatures, but we shall have to prepare additional calibration solutions and analyze them isotopically.

BIBLIOGRAPHY

Anderson, D. E., and Graf, D. L., Ionic diffusion in naturally-occurring aqueous solutions: use of activity coefficients in transition-state models: Geochim. Cosmochim. Acta, 42, 251-262, 1978.

Bennett, R. H., Bryant, W. R., and Keller, G. H., Clay fabric and geotechnical properties of selected submarine sediment cores from the Mississippi Delta: U. S. National Oceanic and Atmospheric Adm., Prof. Paper 9, Rockville, Md., 86 pp., 1977.

Benzel, W. M., Cation exchange properties of montmorillonite at temperatures simulating subsurface environments: M. S. Thesis, Dept. of Geology, University of Illinois at Urbana-Champaign, 45 pp., 1978.

Calladine, C. R., Overconsolidated clay; a microstructural view: in Proc. Symp. Role of Plasticity in Soil Mechanics (ed., A. C. Palmer), Cambridge Univ. Engg. Dept., 144-160, 1973.

Coplen, T. D., and Hanshaw, B. B., Ultrafiltration by a compacted clay membrane--I. Oxygen and hydrogen isotopic fractionation: Geochim. Cosmochim. Acta, 37, 2295-2310, 1973.

Graf, D. L., X-ray cells for diffraction analysis of flat powder mounts in contact with liquid at elevated temperature and pressure: Amer. Mineralogist, 59, 851-862, 1974.

Graf, D. L., Friedman, Irving, and Meents, W. F., The origin of saline formation waters II. Isotopic fractionation by shale micropore systems: Ill. State Geol. Survey Circ. 393, 32 pp., 1965.

Hitchon, B., and Friedman, I., Geochemistry and origin of formation waters in the western Canada sedimentary basin--I. Stable isotopes of hydrogen and oxygen: Geochim. Cosmochim. Acta, 33, 1321-1349, 1969.

Kharakha, Y. K., and Smalley, W. C. Flow of water and solutes through compacted beds: Bull. Amer. Assoc. Petrol. Geologists, 60, 973-980, 1976.

Mahmood, Arshud, and Mitchell, J. K., Fabric-property relationships in fine granular materials: Clays & Clay Mins., 22, 397-408, 1974.

Martin, R. T., and Ladd, C. C., Fabric of consolidated kaolinite: Clays & Clay Mins., 23, 17-25, 1975.

Meade, R. H., X-ray diffractometer method for measuring preferred orientation in clays: U. S. Geol. Survey Prof. Paper 424-B, pp. B-273-B276, 1961.

Parham, W. E., and Austin, G. S., Clay mineralogy fabric and industrial uses of the shale of the Decorah Formation, southeastern Minnesota: Minnesota Geol. Survey Rept. Inv. 10, 32 pp., 1969.

Rard, J. A., and Miller, D. G., The mutal diffusion coefficients of $Na_2SO_4-H_2O$ and $MgSO_4-H_2O$ at 25° C from Rayleigh interferometry: Jour. Solution Chem., 8, 755-766, 1979.

Rard, J. A., and Miller, D. G., The mutual diffusion coefficients of $NaCl-H_2O$ and $CaCl_2-H_2O$ at 25° C from Rayleigh interferometry: Jour. Solution Chem., 8, 701-716, 1979.

Sofer, Z., and Gat, J. R., Activities and concentrations of oxygen-18 in concentrated aqueous salt solutions: analytical and geophysical implications: Earth Planet. Sci. Letters, 15, 232-238, 1972.

Stephens, M. P., 1974. Ion exchange selectivity of clay under conditions simulating subsurface environments: Ph. D. Thesis, Dept. of Geology, University of Illinois at Urbana-Champaign, 83 pp.

Truesdell, A. H., Oxygen isotope activities and concentrations in aqueous salt solutions at elevated temperatures: consequences for isotope geochemistry: Earth Planet. Sci. Letters, 23, 387-396, 1974.

van Olphen, H., An introduction to clay colloid chemistry: 2nd. ed., Wiley, 1977.